SEASONAL AND LONG-TERM VARIABILITY IN WELL WATER NITRATE-NITROGEN

By

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INTRODUCTION

Nitrate-N contamination of groundwater is of local, regional, and national concern. This interest has come about mainly due to possible health risks associated with consumption of water containing high nitrate-nitrogen (NO_3-N) by infants under 3 months of age. When NO_3-N is ingested by infants, nitrate can be reduced to nitrite by bacteria that live in the digestive tract. Nitrite-N can occupy sites on hemoglobin that would normally carry oxygen. This reduced oxygen carrying capacity of the blood produces symptoms of asphyxiation known as methemoglobinemia, or "blue baby" syndrome. After infants reach an age of 3 to 6 months, the hydrochloric acid levels in their stomachs increase, thereby creating an environment unfavorable for the bacteria.

Methemoglobinemia is readily treated without any known cumulative effects. In most cases, infants can experience full recovery. In the last 30 years, only one infant death in the United States was linked to nitrate poisoning caused from drinking well water (Fedkiw, 1991). The maximum contaminant level or public health standard for NO_3-N in drinking water is 10 mg/L. This level was set many years ago by the Environmental Protection Agency as concentrations below 10 mg/L had resulted in no reported cases of infant methemoglobinemia. Most infants can apparently tolerate NO_3-N in water at levels much higher than 10 mg/L, while other more susceptible infants can begin to exhibit symptoms at levels only slightly higher than 10 mg/L. This standard represents a 10-day

health advisory level. The corresponding 10-day health advisory level for all other age groups is 111 mg/L NO_3-N (Baker et al., 1989). Concerns for adults include the possibility that nitrates could be reduced and compounded with secondary and tertiary amines to form nitrosamines. These compounds have been identified as carcinogens in numerous animals and could be carcinogens in humans. However, no conclusive evidence linking cancer of any type and drinking water exists (Fedkiw, 1991). Despite the tolerance (for NO_3-N in drinking water) exhibited by humans over 6 months of age, 10 mg/L has remained the standard health advisory level.

The issue that groundwater NO_3-N concentrations may have increased over time is not disputed. Nitrate-N occurs naturally in the soil, as it is continually mineralized from the organic fraction of soil by microorganisms. Since the nitrate ion does not readily adhere to the soil surface, it is free to move in the soil solution and the potential for leaching exists. Agricultural chemicals, particularly N fertilizers, have received the bulk of the blame for many increases in groundwater NO_3-N. This allegation is demonstrated in a computer based literature search performed by L.W. Canter that cites numerous references where groundwater NO_3-N was associated with fertilizer use (Canter, 1987).

In order for fertilizers to be directly responsible for groundwater contamination, NO_3-N would have to be leached out of the soil profile. The occurrence of this is preceded by other processes resulting in much higher levels of N removal. Some of these include the following: NH_3 volatilization from surface applied fertilizer, organic immobilization, plant uptake, and denitrification (Mills et al., 1974; Sharpe et al., 1988; Hooker et al., 1980; Aulakh et al., 1984). Assuming that all N sinks are filled, the amount of NO_3-N

available to be leached should be at a minimum. However, improper land management combined with hydrogeological factors and precipitation can result in excess amounts of NO_3-N accumulating and leaching.

McDonald and Splinter (1982) showed that increased fertilizer was associated with increased nitrate in groundwater between 1952 and 1979 in wells less than 30.4 m deep. It must be considered that this time period was the birth of the fertilizer industry and information concerning fertilizer recommendations was not as available as the fertilizer itself. Therefore, it is possible that excess fertilizer was being applied. Keeney (1986) observed groundwater NO_3-N concentrations begin to decline in the early 1980's. Additional data supporting this trend is provided by a long-term analysis performed in Nebraska from 1960-1983. This work showed significantly increased NO_3-N median levels first appearing in 1971, but decreasing levels in the early 80's resulted in the median concentration for 1983 being lower than was predicted (Chen and Druliner, 1988).

Poor N management combined with hydrogeological factors also results in groundwater NO_3-N accumulation. The Big Springs Basin in northeastern Iowa is a major site for groundwater recharge in that area. Numerous sinkholes in the karst topography serve as a direct route for NO_3-N transport to groundwater. In 1984, excess N applied in the basin area averaged 90 kg/ha. This amount was approximately equal to that exported in Big Springs (Keeney, 1986). Precipitation rates can also effect the leaching of applied N. Area studies conducted in Nebraska between 1974 and 1984 documented increases in groundwater NO_3-N for an area classified as highly vulnerable

(Exner and Spalding, 1990). Highly fertilized, irrigated corn production and a depth to water of less than 15.2 m were factors contributing to this classification. Increases in groundwater NO_3-N observed by Keeney (1986) were also for a heavily irrigated area overlying shallow groundwater. Because most NO_3-N sources are at the surface level, one would expect shallow aquifers to be more susceptible to contamination than deeper ones. However, a shallow aquifer does not always guarantee NO_3-N contamination. Results from a study conducted by the United States Geological Survey involving nearly 124,000 wells showed 33% of wells deeper than 30.4 m had NO_3-N concentrations in excess of 10 mg/L (Madison and Brunett, 1985).

Nitrate-N contamination of deeper groundwater can occur where a hydraulic connection and a downward hydraulic gradient exist between shallow and deep aquifers. This results in possible recharge of the deep aquifer with NO_3-N rich water from the shallow aquifer. This is supported by Wall and Magner (1988) who determined that high capacity pumping of deep wells was drawing water downward from overlying aquifers, thus resulting in contamination of the deeper wells. The migration of water through the unsaturated zone of many soils can be quite slow. The time required for inputs of N to reach the groundwater reservoir could be many years. Therefore, N sources present at one time, although obliterated, could still result in NO_3-N contamination of deep wells (Exner and Spalding, 1985).

Denitrification is another factor that must be considered when assuming that shallow wells are more susceptible to leachate contamination. Elevated denitrification in a highly vulnerable area (irrigated cropland, shallow water table) resulted in the majority of 15

wells sampled having concentrations less than 2 mg/L NO_3-N while only 3 wells exceeded 7 mg/L (Fedkiw, 1991).

Non-point source pollution from nitrogen fertilizer application is not the only source of well water contamination. Data from 150 farmstead wells in Kansas reported wells on or within 9.1 m of cropland had a lower average concentration of NO_3-N versus non-cropland wells (Koelliker et al., 1988). The data also pointed out that while fertilization could increase background levels of NO_3-N in groundwater, the level of concentration that results is likely to be less than the maximum contaminant level (10 mg/L). Point sources of NO_3-N were considered to be more likely causes of higher concentrations. Some of the origins of point source contaminants include livestock feedlots, improper well construction and location, and domestic septic disposal systems.

Manure from livestock feedlots has been identified as a predominant source of NO_3-N contamination by various authors. However, NO_3-N is less likely to leach from continuously stocked feedlots than from those which have been abandoned or are used only intermittently (Exner and Spalding, 1985). Continuously stocked feedlots, such as commercial operations, contain constantly accumulating manure where hoof compaction and urine excretion create a surface seal that keeps the surface damp and conducive to nitrogen reduction by preventing movement of large amounts of water through the soil surface. Nitrification is unlikely under such conditions. Conversely, abandoned or intermittently used lots, common on small farmsteads, have manure accumulation that is subject to drying, cracking, nitrification, and leaching.

Inadequate well construction has been strongly correlated with NO_3-N occurrence (FMW Water Project, 1988). Wells containing concrete or clay tile casings have shown higher NO_3-N levels than those with steel or plastic casings. Non-watertight casings make a well a prime candidate for contamination. Hirschi et al. (1993) cited that 30% of large diameter dug or bored wells included in a statewide survey in Illinois had NO_3-N levels in excess of 10 mg/L, while only 9% of drilled wells included in the survey exceeded this level. Large diameter dug or bored wells are particularly vulnerable to contamination because of their design and generally shallow depth. In contrast, deep drilled wells are often not considered vulnerable to contamination, however if only a few feet of the well are cased, then pollutants may seep into the well. Well location is also a major factor in groundwater quality. Wells located in close proximity to landfills, underground storage tanks, fuel storage tanks, and septic systems are probable sites for contamination.

Septic systems in particular are major sources of NO_3-N to groundwater (Canter and Knox, 1985). A 1980 study by the U.S. Environmental Protection Agency estimated that an average of 4.0 kg N/person/year is released to soil via septic systems (USEPA, 1980). Similar figures (3.2 kg N/person/year) were reported by the Minnesota Pollution Control Agency in 1991 (MPCA, 1991). These estimates are based on properly functioning septic systems. A faulty or damaged system would result in much higher amounts of N being released into the soil. Results from a Rhode Island study involving NO_3-N losses from a variety of land practices suggest that replacing production agriculture with unsewered residential development will not markedly reduce NO_3-N losses to groundwater (Gold et

al., 1990). Another study hypothesized that positive trends toward lower NO_3-N concentrations in many rural areas may be the direction of the future since much of nitrate contamination is associated with a combination of poor well siting and construction (Spalding and Exner, 1990).

Many hydrogeologic and source related factors exist which can control the amount, position, and timing of NO_3-N concentration in groundwater. Complex interactions of these factors make it difficult to draw any general inferences about the potential for NO_3-N contamination of groundwater in a particular region. The best approach to determine where NO_3-N contamination exists is through direct sampling and analysis of well water. Fedkiw (1991) noted that NO_3-N sample variances within and between wells in the same locale and between years or seasons is very large. A study in Ohio reported that for a population of 152 wells, a one time finding of a concentration as low as 6 mg/L indicated a 50% chance of at least one reading above 10 mg/L during the year for that same well (Baker et al., 1989). The same study found wells that exceeded 10 mg/L for one sampling date may have median concentrations as low as 2 mg/L. Researchers in Minnesota reported NO_3-N in one well to drop from 30 mg/L in June 1987 to 1 mg/L in March 1988 (Wall and Magner, 1988). Gilliam et al. (1974), and McDonald and Splinter (1982) have also reported NO_3-N levels for a specific well to vary among seasons. This reflects an error associated with seasonal sampling which suggests that one sample is not sufficient to provide conclusive evidence of groundwater quality, and recurrent monitoring of water wells is necessary to most accurately determine NO_3-N concentrations. In another study conducted in Minnesota, the mean NO_3-N concentration

for a group of wells sampled during the period 1982-1984 was higher than the mean concentrations obtained in earlier studies (1965-1978) performed by the USGS on the same wells (Anderson, 1989). However, seasonal fluctuations in mean concentrations observed during the 1982-1984 period were greater than the apparent historical increase in NO_3-N concentration. This generates doubt as to whether or not a real increase took place or if errors stemming from seasonal variation influenced the data interpretation.

Methods used to analyze groundwater samples for NO_3-N can also be a source of error when comparing historical data. Since the 1950's, several analytical methods have been used to determine NO_3-N in groundwater. Each of these methods has its own inherent random and bias errors. Direct numerical comparison between data analyzed using two different procedures without assessing the proper errors could be inaccurate. Various authors including Schepers et al. (1991), Walters and Malzer (1990), and Webster et al. (1986), have evaluated the impacts of continuous cropping systems where N fertilizers have been applied annually without considering the analytical errors associated with these estimates. DeWalle and Schaff (1980), and Olson (1974), have reported agriculture related increases in groundwater NO_3-N concentrations spanning time periods of up to thirty years without addressing the effects of changing analytical methods on their results.

Another possible source of error when comparing historical data is storage of the sample. Current protocol requires that water samples being analyzed for NO_3-N be cooled to 4-10° C for transport or analyzed immediately in the field (Scalf et al., 1981). Recommended maximum holding time for samples is 48 hours. This sample handling protocol is to minimize any biological transformations that may be taking place. Data

compiled several years ago which provide benchmark levels for historical comparisons may include samples which were taken without observing these guidelines.

Without adequately assessing all the statistical parameters associated with an independent estimate, researchers are at risk of making scientifically invalid conclusions about changes in NO_3-N concentrations. The objectives of this research were to determine the errors associated with analytical procedure, seasonal sampling, and storage method for well water NO_3-N analysis, and to identify where significant changes have taken place using historical groundwater data.

MATERIALS AND METHODS

Seventy-five water wells in Garfield, Grant, and Kingfisher counties in north central Oklahoma were selected for comprehensive sampling. These wells were selected on the basis that NO_3-N data collected during the time period 1953-1972 was available to serve as benchmark levels (Bingham and Bergman, 1980; Dover, 1953; U.S.G.S., 1993). The major groundwater basins underlying these counties are alluvium and terrace deposits. These deposits are found along rivers and streams as unconfined aquifers and consist of interfingerings of sand, sandy clay, clay, and gravel. Water quality is affected by nearby streams, however, overall water quality is good and the water can be used for domestic, irrigation, industrial, and municipal purposes. Average annual precipitation for this area ranges from 711-864 mm while the average annual evaporation rates range from 1500-1600 mm. This relationship results in evapotranspiration removing approximately 80% of Oklahoma's water from availability for immediate use (Barnett, 1984). These counties also have substantial agricultural activity associated with continuous wheat production and N fertilization.

Tax records obtained from the three counties were used to determine current ownership of the property on which each well was located. The owners were contacted and informed about the experiment. Due to changes which had taken place since the original data was compiled, several of the wells no longer existed. In many cases,

verification of well authenticity was also difficult. The wells sampled during the benchmark period were identified by legal description only. This recognized a 0.65 to 2.59 square km area on which the specific well was located. Many of these sections of land contained numerous water wells. Several cooperators were able to verify prior samplings based on personal knowledge, family records, or inquiries of previous land owners. Information regarding the age of particular wells made proper well selection possible at many locations. Consequently, the number of wells to be sampled was reduced to 50 and permission was obtained from the well owners or leasing individuals to begin quarterly well water sampling beginning in the fall of 1993. The sites on which these wells were located represented a variety of soil types and land uses as defined in Table 1. The group of wells included both dug and drilled wells having an average total depth of 14.6 m and an average depth to water of 6.4 m. Water samples were obtained each season (fall, winter, spring, summer) from September 1993 through July 1995.

In order to obtain a representative groundwater sample, it is desirable to take the sample directly from the aquifer. However, 39 of the 50 wells contained in-place semi-permanent mounted pumps which limited the options available for groundwater sampling. These wells were pumped for an amount of time adequate to remove several bore volumes of water from the well so that water samples collected reasonably represented that of the aquifer (Scalf et al., 1981). Of the 11 other wells, 7 were collected via windmills and 4 were collected using a teflon bailer. The bailer was sanitized in the field with de-ionized water following each use (Davis et al., 1993). All samples were handled using established sampling protocol (Barcelona et al., 1987). For each sampling

date, four samples were collected in 250 ml plastic bottles from each well whereby two were stored according to current groundwater sampling procedures by freezing the samples immediately using an ice chest containing dry ice, and two were stored at ambient temperatures for 1-2 days until analysis was performed (protocol common when much of the benchmark data was collected). Frozen samples were allowed to thaw to room temperature before analysis was performed.

Frozen and non-frozen samples were analyzed using two methods. One method utilized was phenoldisulfonic acid (Bremner, 1965; Chapman and Pratt, 1961; Snell and Snell, 1949), one of the earliest detection methods used for NO_3-N analysis. Phenoldisulfonic acid was also the method of choice when most of the benchmark data was analyzed. This colorimetric procedure is tedious, time consuming, and has been found to be subject to several interferences. Nitrate-N concentration was also determined using the 'Lachat-Quickchem' automated flow injection system which employs automated cadmium reduction of nitrate to nitrite and measurement of nitrite by the Griess-Ilosvay method (Henrickson and Selmer-Olsen, 1970; Jackson et al., 1975; Keeney and Nelson, 1982). This procedure is currently used by many industrial and public laboratories. Statistical analysis of data was performed using procedures outlined by the SAS institute (SAS, 1990). A 'split-plot' in space and time analysis of variance model was used to assess the effect of sampling (4 seasons * 2 years), method of storage (frozen versus non-frozen), method of analysis (phenoldisulfonic acid versus cadmium reduction), and main effect interactions.

RESULTS AND DISCUSSION

Wells with missing observations were deleted from the analysis of variance (AOV) in order to provide equal observations per cell. However, these wells were included in the discussion of changes within individual wells. No significant differences were detected in either sampling or storage main effects. However, the effect of analytical method on NO_3-N concentration was significant ($p < .02$). Highly significant sampling by method of analysis ($p < .007$) and sampling by storage ($p < .0001$) interactions were observed (Table 2). These interactions among sampling, storage, and method restrict the accuracy with which individuals can make direct numerical comparisons between NO_3-N data obtained using one combination of variables and NO_3-N data obtained using another combination. The overlapping errors associated with combining independent variables implied that the benchmark data would have had a different statistical error associated with it than data collected from the same wells in the last two years.

A pooled within well variance estimate for the benchmark data was derived by taking the square root of the mean square error from an analysis of variance using NO_3-N values obtained from non-frozen samples analyzed using phenoldisulfonic acid. Five wells were excluded from this AOV as they had extremely large standard deviations among samplings and were obviously skewing the distribution. A similar estimate was made for frozen samples analyzed using cadmium reduction, again eliminating outliers from the

analysis. Although certain wells were not included in either AOV, the changes within each of these wells has been included in the discussion. Pooling these error terms produced the proper variance estimate to be used for direct comparisons between benchmark data (collected several years ago using non-frozen samples analyzed by the phenoldisulfonic acid procedure) and current data (frozen samples analyzed by cadmium reduction) from the same well.

Significant changes in NO_3-N for each well were determined by calculating a predicted Z value for each well using the pooled variance estimate appropriate for making direct comparisons between independent values from benchmark and current data (Table 3). Four of the 50 wells sampled in the study had no benchmark NO_3-N data available, therefore, only changes from 46 wells are reported. Direct comparisons of data for each well, disregarding statistical analysis, would have resulted in increases being observed to have taken place in 35 of the 46 wells (76%). Using a pooled error term generated by method and storage, significant increases in well water NO_3-N were found in only 14 wells (30%), while 5 wells (11%) showed significant decreases and 27 wells (59%) showed no significant change over time (Figure 1). The least significant difference ($LSD_{0.05}$) using a pooled error term (by method and storage) was 8.50 mg/L. This value is large when used to discuss changes in well water NO_3-N, but when comparing values obtained using independent sampling and testing procedures, the chance of incorrectly declaring significant changes is also obviously large.

The procedure used to determine the smallest significant change in well water NO_3-N was a comparison between benchmark data and mean NO_3-N values obtained using non-

frozen samples analyzed using phenoldisulfonic acid. By imitating the procedure (storage and analysis methods) by which the benchmark data was collected, a common error rather than a pooled error term could be used. The use of this common error resulted in much smaller significant differences being detected ($LSD_{0.05} = 4.89$). Significant changes detected using this comparison are found in Table 4. By being able to declare much smaller differences significant, wells showing increases went up to 52%, wells showing decreases changed to 13%, and the percent of wells showing no significant change dropped to 35% (Fig 1). The comparison between benchmark data and current data obtained by imitating the benchmark procedures (non-frozen, phenoldisulfonic acid) was used for the following discussion of NO_3-N changes within wells.

Of the 24 wells which have shown a historical increase, only 17 exceed the maximum contaminant level of 10 mg/L (#'s 2, 3, 5, 7, 8, 11, 12, 13, 18, 20, 24, 31, 33, 39, 41, 44, 50). Of these 17 wells, 8 (#'s 2, 13, 14, 24, 33, 39, 44, 50) have been identified as being contaminated by point source pollution. Wells 13, 14, 24, and 44 were all located on highly vulnerable farmsteads. The soil texture for these four sites was fine sand to sandy loam and the average depth to groundwater was 5.2 m. All of these wells were located in close proximity to a livestock corral which frequently contained livestock. This combination of factors made these wells prime candidates for animal waste NO_3-N contamination. Well 2 was a shallow hand dug well that has been recharged from nearby surface streams which traverse a pasture stocked with several head of cattle. Nitrate-N levels in these surface streams (collected in April, 1995) were approximately equal (10.90

mg/L) to those found in the well water samples, suggesting that the well water was being contaminated at the surface rather than underground.

Wells 33, 39, and 50 were probably being contaminated as a result of poor well construction. Well 39 was a large diameter hand dug well. This type of well is vulnerable to contamination from sources near the well because of its design and shallow depth to aquifer (5.5 m). Well 39 was located at an urban residence and was not associated with any type of agricultural production, however it contained the third highest mean NO_3-N concentration of all wells sampled. The area on which well 33 was located was occupied by several oil pumping units and drilling rigs. Well 33 was originally drilled in an unsuccessful attempt to find oil. The initial bore size was 20 cm in diameter. When no oil was discovered, a 13 cm casing was installed to utilize the site as a water well. The remaining 7 cm was never filled in, resulting in any surface contamination having direct access to the groundwater system. This well was also located in the immediate vicinity of an excessively manure-fertilized garden and a septic system. Well 50 was a 15 m drilled well, but had only been cased to 6 m with open bore extending the remainder of the well depth. The well was also located on a downhill gradient from the residence septic system and a corral. Wells 33 and 50 had the highest NO_3-N concentrations of all wells sampled (86 and 62 mg/L respectively). In order to ensure that these wells were point source contaminated, surrounding wells were sampled for both sites. For both locations, the surrounding wells failed to show any signs of contamination concluding that NO_3-N levels in wells 33 and 50 were indeed from point sources.

If leaching of surface applied nitrogen fertilizers was the source of contamination, then it would be expected that the more shallow aquifers would show greater increases than the deeper ones. However, no relationship between depth to aquifer and NO_3-N concentration existed for the wells showing significant increases excluding those contaminated by point sources (Figure 2). Similarly, no relationship was found between the average depth to aquifer and well water NO_3-N for all wells excluding those contaminated by point sources in either the benchmark years or the past two years (Figure 3). Since fertilizer usage has increased steadily since the early 1950's, NO_3-N leaching from the excessive use of N fertilizers over this historical period, should have resulted in higher NO_3-N concentrations in the shallower wells. If this were the case, regression equations with well water NO_3-N dependent upon depth to the aquifer (on these extremely shallow wells) should have contained negative slopes. Because this was not found, it is unlikely that leaching of surface applied nitrogen fertilizers was the source of increased NO_3-N concentrations in this population of wells. Hydrogeological characteristics, evapotranspiration rates, and biological transformations of NO_3-N limit the potential for leaching in this area. The seasonal fluctuations for this group of wells averaged 2.23 mg/L over the two year sampling period. Excluding differences in the fall samplings, well water NO_3-N levels tended to increase from winter to spring to summer with an average change over season in excess of 1 mg/L (Figure 4).

Of the 6 wells (#'s 1, 4, 19, 25, 26, 38) which have shown a significant decrease, 3 (#'s 1, 4, 38) have been identified as prior sites of point source contamination. Wells 1 and 4 were both located on sites that were poultry production areas when the benchmark

data was collected. Well 1 was a 9 m deep hand dug well which was pumped using a windmill. At the time of the original sampling, the well was uncovered and the population of chickens in a concentrated area was in the thousands. Since then, the chickens have been removed and the well has been covered with a concrete slab. Well 4 has become a residence well, and the chickens have been gone for several years, resulting in decreased NO_3-N values. Well 38 was a hand dug well when it was sampled in 1950. Since that time, it has been properly cased and secured, thus NO_3-N in the water has significantly decreased. Wells 25 and 26 were both located on the same section of land. The land was irrigated cropland overlying a shallow aquifer which may explain why the NO_3-N levels have remained >10 mg/L over the years. However, no information was obtainable regarding the history of the area to determine the source of high benchmark levels of NO_3-N, nor was any historical information available for well 19. All three of these wells were assumed to be previously point source contaminated as their NO_3-N concentrations grossly exceeded the average for that time period.

The average NO_3-N concentration for the population of wells, excluding those which have been point source contaminated, over the past two years was 8.40 mg/L. The average benchmark NO_3-N concentration excluding previously contaminated wells was 2.90 mg/L. The average time span between benchmark and current sampling dates for all wells was 38 years. This reflects a 0.14 mg/L/yr increase occurring for this population of wells at the 95-percent confidence level. This figure very closely agrees with Chen and Druliner, 1988, who found NO_3-N concentrations in Nebraska groundwater to be increasing at a rate of 0.12 mg/L/yr.

CONCLUSIONS

Significant interactions were found to exist among seasonal sampling, sample storage, and method of analysis for well water NO_3-N. This places individuals at risk of drawing incorrect conclusions about significant changes which may have taken place when making direct numerical comparisons between historical NO_3-N levels (obtained from analyzing non-frozen samples using phenoldisulfonic acid) and current NO_3-N levels (obtained from analyzing frozen samples using automated cadmium reduction). By identifying the statistical errors associated with the collection of independent samples, more reliable determinations about changes in NO_3-N can be made. The variance estimate calculated for non-frozen samples analyzed using phenoldisulfonic acid was 2.49 mg/L. This is the error that should be assigned to any NO_3-N value obtained using these procedures when making historical comparisons. No relationship was found to exist between depth to aquifer and well water NO_3-N for the benchmark population, the current population, or the wells which have shown significant increases. Since fertilizer use has increased since the 1950's, this further supports the idea that leaching of surface applied fertilizers has not been a source of increased groundwater NO_3-N for this population of wells in north central Oklahoma.

Table 1. Soil type, major land use and average depth to aquifer for each well in Grant, Garfield, and Kingfisher Counties, OK.

WELL	SOIL TYPE	MAJOR LAND USE	DEPTH TO AQUIFER (m)
1	KINGFISHER SILT LOAM, 3 TO 5 % SLOPE	CROPLAND	5.1
2	RENFROW CLAY LOAM, 1 TO 3 % SLOPE	CROPLAND	5.7
3	NORGE FINE SANDY LOAM, 0 TO 1 % SLOPE	CROPLAND	5.7
4	PORT SILT LOAM, 0 TO 1 % SLOPE	RANGELAND	5.7
5	KINGFISHER SILT LOAM, 3 TO 5 % SLOPE	CROPLAND	10.6
6	PORT CLAY LOAM, 0 TO 1 % SLOPE	CROPLAND	10.6
7	PORT CLAY LOAM, 0 TO 1 % SLOPE	CROPLAND	10.6
8	PRATT LOAMY FINE SAND, UNDULATING	CROPLAND	6.6
9	PRATT LOAMY FINE SAND, UNDULATING	CROPLAND	8.2
10	PRATT LOAMY FINE SAND, HUMMOCKY	CROPLAND	7.6
11	LINCOLN LOAMY FINE SAND	IRRIGATED PASTURELAND	3.0
12	NORGE-SLICKSPOT COMPLEX, 1 TO 3 % SLOPE	CROPLAND	5.1
13	NORGE FINE SANDY LOAM, 0 TO 1 SLOPE	CROPLAND	4.5
14	PRATT LOAMY FINE SAND, HUMMOCKY	RANGELAND	5.1
15	PRATT LOAMY FINE SAND, UNDULATING	CROPLAND	8.5
16	PRATT LOAMY FINE SAND, UNDULATING	CROPLAND	3.3
17	DOUGHERTY-EUFALA LOAMY FINE SAND	IRRIGATED CROPLAND	8.8
18	CARWILE LOAMY FINE SAND	CROPLAND	7.6
19	SHELLABARGER FINE SANDY LOAM, 5 TO 8 % SLOPE	RANGELAND	7.9
20	DOUGHERTY-EUFALA LOAMY FINE SAND, UNDULATING	CROPLAND	7.9
21	PRATT LOAMY FINE SAND, HUMMOCKY	CROPLAND	5.4
22	DOUGHERTY-EUFALA LOAMY FINE SAND, HUMMOCKY	PASTURELAND	5.4
23	DOUGHERTY-EUFALA LOAMY FINE SAND, UNDULATING	CROPLAND	10.0
24	CARWILE LOAMY FINE SAND	CROPLAND	4.8
25	DOUGHERTY-EUFALA LOAMY FINE SAND	IRRIGATED PASTURELAND	3.9
26	DOUGHERTY-EUFALA LOAMY FINE SAND	IRRIGATED PASTURELAND	3.9
27	ALLUVIAL AND BROKEN LAND	CROPLAND	5.1
28	EUFALA FINE SAND	CROPLAND	3.3
29	PRATT LOAMY FINE SAND, UNDULATING	RANGELAND	5.1
30	DOUGHERTY-EUFALA LOAMY FINE SAND, UNDULATING	CROPLAND	5.4
31	SHELLABARGER FINE SANDY LOAM, 1 TO 3 % SLOPE	CROPLAND	6.0
32	PORT CLAY LOAM	CROPLAND	5.4
33	ERODED CLAYEY LAND	RANGELAND	11.5
34	KIRKLAND SILT LOAM, 0 TO 1 % SLOPE	CROPLAND	5.7
35	PORT SILT LOAM, 0 TO 1 % SLOPE	CROPLAND	5.4
36	POND CREEK SILT LOAM, 0 TO 1 % SLOPE	CROPLAND	5.4
37	DRUMMOND SOILS	RANGELAND	3.3
38	GRANT-NASH SILT LOAM, 5 TO 8 % SLOPE	RANGELAND	9.1
39	SHELLABARGER-CARWILE FINE SANDY LOAM	URBAN/BUILT UP LAND	5.4
41	RENFROW-VERNON COMPLEX, 3 TO 5 % SLOPE, ERODED	CROPLAND	5.4
42	KIRKLAND-RENFROW SILT LOAM, 1 TO 3 % SLOPE	CROPLAND	5.4
43	KIRKLAND SILT LOAM, 0 TO 1 % SLOPE	CROPLAND	5.1
44	MENO LOAMY FINE SAND, UNDULATING	RANGELAND	6.0
45	POND CREEK SILT LOAM, 0 TO 1 % SLOPE	CROPLAND	8.2
46	GRANT SILT LOAM, 3 TO 5 % SLOPE, ERODED	CROPLAND	5.4
48	YAHOLA FINE SANDY LOAM, OCCASIONALLY FLOODED	RANGELAND	3.0
49	QUINLAN-WOODWARD LOAM, 3 TO 12 % SLOPE	RANGELAND	9.1
50	RENFROW SILTY CLAY LOAM, 2 TO 5 % SLOPE, ERODED	CROPLAND	7.9
51	McLAIN-DRUMMOND SILT LOAM, RARELY FLOODED	RANGELAND	9.1
52	KIRKLAND SILT LOAM, 1 TO 3 % SLOPE	CROPLAND	4.5

Table 2. Split-plot in space and time analysis of variance model and means for well water NO_3-N, 1993 - 1995.

Source	df	Mean Squares	F value	Pr > F
Well	23	1750.49	53.12	.0001
Sampling	7	32.50	0.99	.4430
Well*Sampling	161	32.95		
Storage	1	0.03	0.01	.9360
Sampling*Storage	7	27.64	5.50	.0001
Well*Storage(Sampling)	184	5.02		
Method	1	54.65	5.23	.0228
Sampling*Method	7	29.56	2.83	.0070
Storage*Method	1	20.77	1.99	.1594
Sampling*Storage*Method	7	15.09	1.44	.1863
Residual Error	368	10.45		

df - degrees of freedom

---------- Means for well water NO_3-N, 1993-1995 ----------

Means	NO_3-N	SD
Sampling		
Fa93	9.82	5.36
Fa94	9.07	5.40
Sp94	9.80	5.46
Sp95	9.94	6.69
Su94	10.06	7.43
Su95	10.28	5.19
Wi93	9.26	5.18
Wi94	9.49	6.05
Storage		
Frozen	9.72	5.91
Non-frozen	9.71	5.88
Method		
Cadmium reduction	9.90	6.82
Phenoldisulfonic acid	9.53	4.79

SD - standard deviation

Table 3. Changes in well water NO_3-N as determined by comparing benchmark samples (non-frozen, phenoldisulfonic acid) with current samples from the same wells that were frozen and analyzed using cadmium reduction.

Well No.	Benchmark NO_3-N	Current NO_3-N	Sig.
	----------mg/L----------		
1	20.70	19.28	ns
2	0.77	8.68	ns
3	0.02	11.52	++
4	42.75	2.50	**
5	0.11	10.33	+
6	0.18	2.78	ns
7	0.02	14.67	++
8	0.14	11.03	+
9	6.75	9.20	ns
10	8.78	10.82	ns
11	0.00	0.71	ns
12	0.15	11.00	+
13	0.31	34.64	++
14	0.29	15.33	++
16	11.25	15.14	ns
18	5.85	13.72	ns
19	36.00	11.10	**
20	3.83	11.91	ns
21	0.29	4.76	ns
23	2.70	10.38	ns
24	1.31	16.55	++
25	67.50	21.09	**
26	38.25	20.90	**
28	2.25	4.47	ns
29	4.50	6.17	ns
30	3.60	3.51	ns
31	5.85	16.74	+
32	0.77	3.27	ns
33	2.70	99.43	++
34	1.91	7.58	ns
35	2.00	7.24	ns
36	1.13	4.46	ns
37	1.24	5.38	ns
38	22.50	1.31	**
39	1.40	44.27	++
41	6.98	15.68	+
42	6.75	1.32	ns
43	0.38	1.20	ns
44	2.25	16.79	++
45	1.76	6.49	ns
46	3.38	4.44	ns
48	0.02	1.35	ns
49	1.91	0.69	ns
50	3.38	92.92	++
51	13.50	12.70	ns
52	5.85	0.61	ns

**, * - significant decrease at 0.01 and 0.05 probability levels respectively, ++, + - significant increase at 0.01 and 0.05 probability levels respectively, ns - no significant change, 30% significant increase, 11% significant decrease, 59% no significant change

Table 4. Changes in well water NO_3-N as determined by comparing benchmark samples (non-frozen, phenoldisulfonic acid) with current samples from the same wells that were non-frozen and analyzed using phenoldisulfonic acid.

Well No.	Benchmark NO_3-N	Current NO_3-N	Sig.
	mg/L		
1	20.70	15.57	*
2	0.77	12.25	++
3	0.02	10.67	++
4	42.75	6.05	**
5	0.11	10.51	++
6	0.18	5.56	+
7	0.02	12.95	++
8	0.14	16.03	++
9	6.75	9.08	ns
10	8.78	8.93	ns
11	0.00	3.79	ns
12	0.15	10.14	++
13	0.31	25.98	++
14	0.29	14.06	++
16	11.25	15.14	ns
18	5.85	13.75	++
19	36.00	10.23	**
20	3.83	10.90	++
21	0.29	5.87	+
23	2.70	8.86	+
24	1.31	13.22	++
25	67.50	14.81	**
26	38.25	12.57	**
28	2.25	3.76	ns
29	4.50	6.42	ns
30	3.60	5.43	ns
31	5.85	16.27	++
32	0.77	4.86	ns
33	2.70	85.87	++
34	1.91	7.80	+
35	2.00	7.76	+
36	1.13	5.34	ns
37	1.24	6.40	+
38	22.50	3.21	**
39	1.40	42.37	++
41	6.98	12.28	+
42	6.75	3.62	ns
43	0.38	3.82	ns
44	2.25	14.10	++
45	1.76	6.92	+
46	3.38	4.98	ns
48	0.02	4.00	ns
49	1.91	4.04	ns
50	3.38	61.94	++
51	13.50	8.66	ns
52	5.85	3.54	ns

**, * - significant decrease at 0.01 and 0.05 probability levels respectively, ++, + - significant increase at 0.01 and 0.05 probability levels respectively, ns - no significant change, 52% significant increase, 13% significant decrease, 35% no significant change

Figure 1. Changes in well water NO_3-N determined using phenoldisulfonic acid on non-frozen samples and cadmium reduction on frozen samples

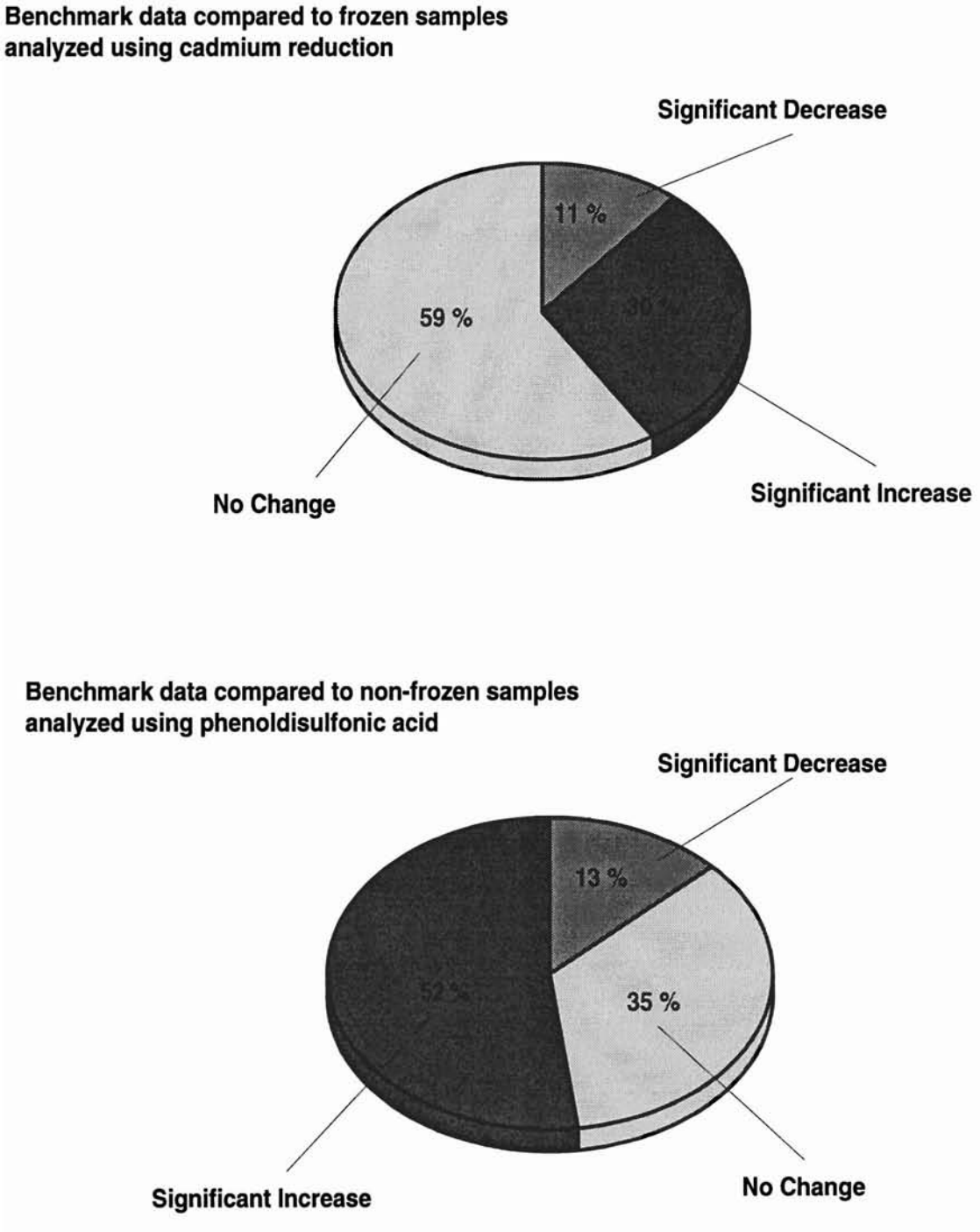


Figure 2. Simple linear regression of changes in well water NO_3-N on the average depth to aquifer for wells showing a significant increase, excluding those which have been point source contaminated.

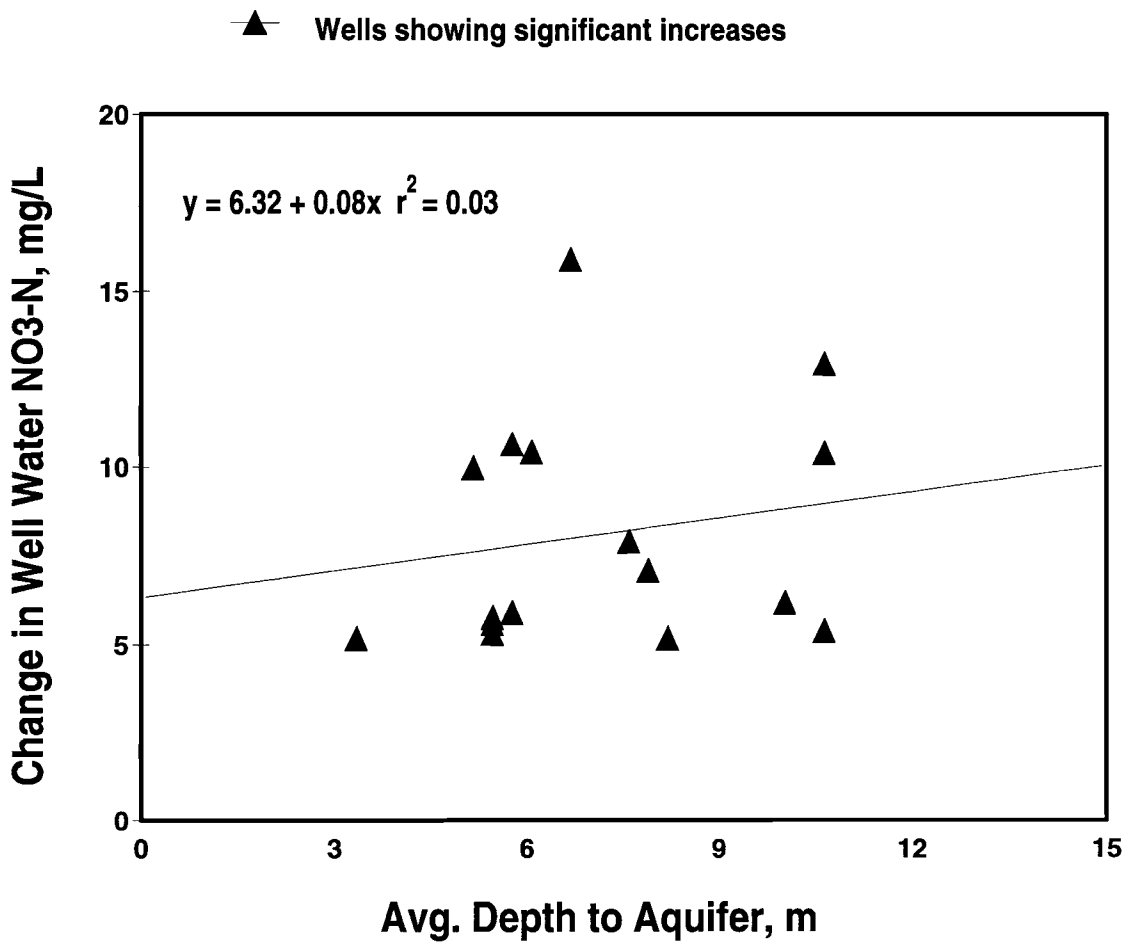


Figure 3. Simple linear regression of well water NO_3-N on the average depth to aquifer for benchmark and current data, excluding wells which have been point source contaminated.

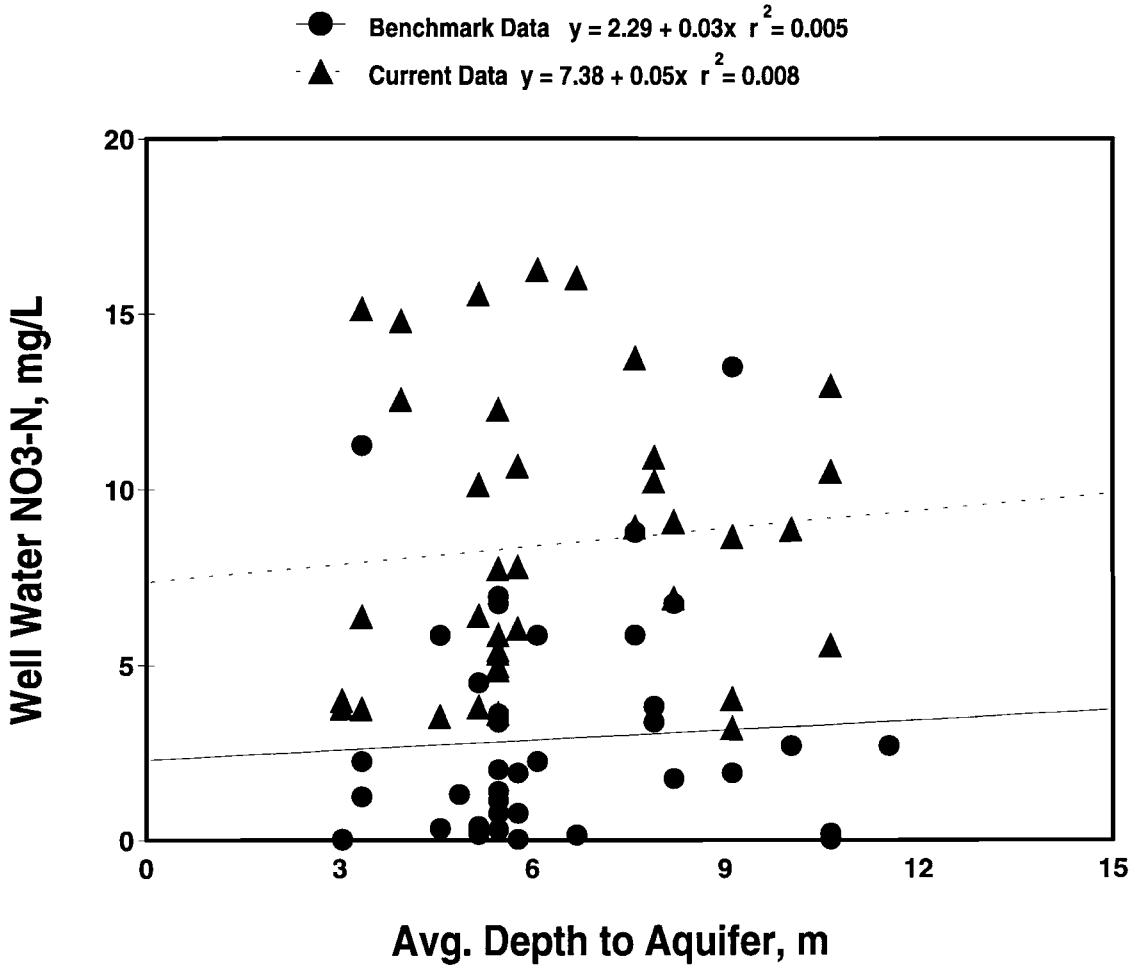
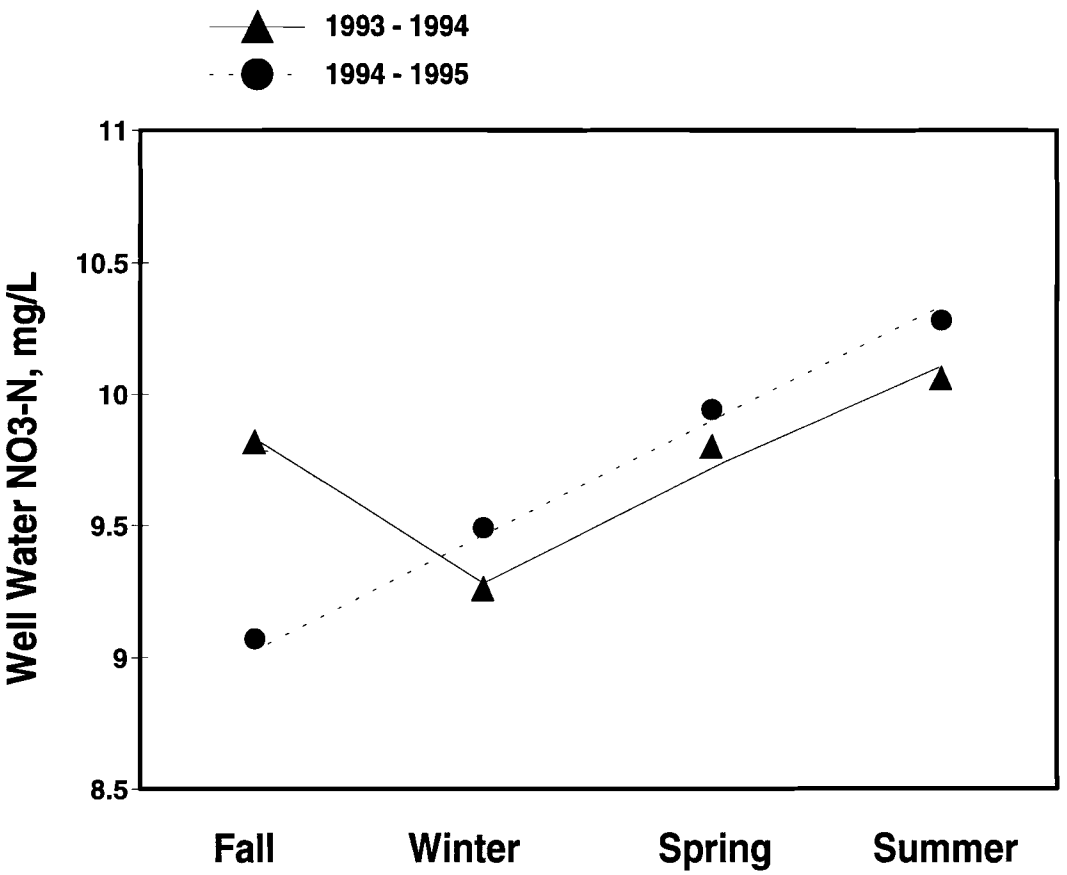


Figure 4. Changes in well water NO_3-N over seasons for samplings fall 1993 to summer 1994 and fall 1994 to summer 1995.



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